# *On the Proximity of Atoms in Gaseous Molecules.*

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1. In a recent note* I have called attention to the degree of correspondence between W. L. Bragg's† estimates (based on X-ray crystal measurements) of the dimensions of certain atoms, and those deduced by means of the kinetic theory of gases from determinations of viscosity. I was not then fully aware of the modern work of Chapman‡ in relation to the latter subject, and made calculations by means of a formula which has been definitely superseded. The result was that the comparison gave only qualitative agreement. A closer examination of the data, in the light of Chapman's results, together with a new aspect of the matter which forms the main subject of the present paper, reveals certain interesting facts regarding the probable arrangement of atoms in molecules, and, in addition, leads to substantial *quantitative* agreement with Bragg's values.

2. From the very close agreement between the values of the atomic radius calculated by means of Chapman's formula,§ and from van der Waal's law, there appears now to be no room for doubt that, in the case of monatomic gases, at any rate, the atoms, when in thermal agitation, behave like hard spheres which exert mutual attraction on one another. It is also evident that the *absolute* diameters of these spheres are now known with considerable accuracy, sufficient to justify quoting to three significant figures. They are given for four monatomic gases in column 3 of Table I for comparison with Bragg's values, which appear in column 2. They differ to a slight extent from those calculated by Chapman himself, owing to the adoption in the present calculation of Millikan's‖ recent value $2{\cdot}705 \times 10^{19}$ for the number of molecules per cubic centimetre at N.T.P. This differs by about 2 per cent. from that used by Chapman, and the substitution results in an increase of about 1 per cent. in the estimated atomic diameter.¶

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* A. O. Rankine, 'Phil. Mag.,' vol. 40, p. 516 (October, 1920).

† W. L. Bragg, 'Phil. Mag.,' vol. 40, p. 169.

‡ S. Chapman, 'Phil. Trans.,' A, vol. 216, p. 279.

§ *Loc. cit.*, p. 347.

‖ R. A. Millikan, 'Phil. Mag.,' vol. 34, p. 1.

¶ It may be pointed out that the formula obtained by Chapman upon the basis above-mentioned leads to values of the molecular dimensions which are independent of temperature. In this respect, among others, it is superior to those derived from

Table I.

| Gas. | Atomic diameter. | | Ratio $(d/\sigma) = K$. |
|---|---|---|---|
| | From crystal measurements, $2d$ (cm. × $10^{-8}$). | From viscosity measurements, $2\sigma$ (cm. × $10^{-8}$). | |
| Neon | 1·30 | 2·35 | 0·553 |
| Argon | 2·05 | 2·87 | 0·714 |
| Krypton | 2·35 | 3·19 | 0·737 |
| Xenon | 2·70 | 3·51 | 0·769 |

W. L. Bragg regards his values as measures of the diameters of the outer electron shells of the respective atoms, and it will be seen that, from this point of view, the moving atoms of a gas do not approach so closely during an encounter that even the outer electrons intermingle. The atom, in so far as collision is concerned, is to be regarded as a hard elastic sphere of radius $(\sigma)$ quite definitely greater than the distance $(d)$ between the centre of the atom and its outer electrons. The ratios in column 4 show that the relation between these two radii is not one of strict proportionality, but depends on the particular type of atom.

3. When we come to consider the case of diatomic molecules—as, for example, in chlorine gas—we are met with the difficulty that we are no longer entitled to regard the molecule as a sphere. Hitherto, it has been customary to regard it as such, and obtain, by the formula which is strictly applicable to single atoms only, an average atomic diameter. In this paper an attempt is made to take into account the well-recognised fact that diatomic molecules are not completely symmetrical. Chapman's viscosity formula, in common with all previous ones, gives a means of calculating, not the atomic radius $(\sigma)$ directly, but the quantity $\pi\sigma^2$, which is the area presented as a target by the atom to other atoms approaching from all possible directions. The author suggests that in applying the formula to molecules consisting of two atoms, while the calculation of the value of $\sigma$ has no definite meaning, it is still possible to obtain a quantity equivalent to $\pi\sigma^2$, which will now represent the mean area which the molecule presents as a target for all possible orientations. We are not, however, justified in going further unless we know the actual shape of the molecule. It happens that the Lewis-Langmuir theory of atomic and

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earlier theories in which the molecules were regarded as free from mutual attractions. The dimensions used in this paper are derived from Chapman's formula, and have, therefore, a perfectly definite significance.

molecular constitution, supported as it is by so many experimental results, provides substantial ground for specifying the shape of a molecule in relation to the atoms of which it is composed. According to this theory we should regard an atom of chlorine as being identical in arrangement with an atom of argon, except that its atomic number (or nuclear charge) is 17 instead of 18, and that, consequently, it lacks one electron in the outer shell required to complete the stable arrangement of eight outer electrons occurring in argon. Stability is secured in gaseous chlorine by the combination together of the atoms in pairs, thus forming diatomic molecules. In each pair two outer electrons are held in common, and, apart from possible distortion arising from such sharing, a chlorine molecule may be regarded as having the size and shape of two argon atoms in contact, *i.e.*, with the outer electron shells touching each other. Gaseous bromine is similarly related to double krypton atoms, and iodine to xenon. In the case of neon, the corresponding element is fluorine, for which there are no viscosity data in existence, but we may go one step further and make the comparison with oxygen. The atom of this gas has two less electrons than neon in the outer electron shell, but, in forming the molecule $O_2$, the pair of oxygen atoms share four outer electrons. Thus, with the restrictions already mentioned, an oxygen molecule has the same size and shape as two neon atoms with their outer electron shells coincident.

The purpose of what follows is to test the validity of this view, making use of the combined results of X-ray crystal measurements and viscosity measurements of atomic and molecular dimensions. To be precise, we shall, for example, construct a hypothetical molecule by placing two argon atoms with their outer electron shells coincident, *i.e.*, with their centres separated by the distance 2·05 Å., derived from crystal measurements. We shall then calculate what mean area (from the point of view of molecular collision) we should expect such a molecule to have, and compare it with the actual mean area of a chlorine molecule, deduced from the viscosity data of that gas. Identity between these two values and between values obtained similarly for the three other pairs of gases already mentioned, will justify the conclusion that the Lewis Langmuir view is substantially correct. It will at the same time—and this is equally important—establish quantitative agreement between the estimates of atomic dimensions derived from methods so different as the X-ray examination of crystals and the measurement of the viscosity of gases.

4. Consideration of Table I will make it clear that if, for example, two argon atoms have their outer electron shells coincident, the spheres representing their behaviour on the kinetic theory will overlap. For the centres are

then 2·05 Å. apart, and the kinetic theory diameter is 2·87 Å., a magnitude considerably greater. The same remark applies to the other monatomic gases, although the extent of overlapping varies from case to case. The question we have to answer is how such a pair will behave, in mutual collision with other pairs, from the point of view of kinetic theory. The hypothetical molecule so constituted will evidently be symmetrical about the line joining the atomic centres, and it will have a shape which we will consider in detail presently. Viewed from a direction making an angle $\theta$ with the symmetrical axis, it will present a certain area A, depending on the shape assigned to the molecule. Since all orientations of the axis are equally probable in thermally agitated molecules, the angle $\theta$ will occur with a proportional frequency $\sin\theta . d\theta$. Thus the mean area presented by the molecule will be

$$\bar{A} = \int_0^{\pi/2} A \sin\theta \, . \, d\theta. \qquad (1)$$

This quantity, $\bar{A}$, will be equivalent to the expression $\pi\sigma^2$, which appears in the viscosity formula derived from the consideration of monatomic molecules as hard, elastic spheres. The evaluation of $\bar{A}$ will enable us to perform the comparison contemplated, viz., to test the dimensional equality of a hypothetical pair of contiguous argon atoms and a chlorine molecule, and the corresponding cases, neon-oxygen, krypton-bromine, and xenon-iodine.

5. We have now to consider the shape which we may assign to the molecule. It is known from Chapman's work on kinetic theory that, in the case of monatomic molecules, the model which fits in best with experimental facts is a hard elastic sphere* of definite radius $\sigma$. By analogy it is reasonable to suppose that a molecule, although not spherical, does behave in collision like a hard elastic body of some definite shape. That shape must evidently bear some relation to the value of $\sigma$ for the participating atoms and to the distance apart, *d*, of the atomic centres. There are no means available at present for the precise calculation of the shape. All we can do is to assume probable shapes, and find which leads to the most consistent results. I have worked out these for three shapes for the contemplation of which there appear to be sound reasons, and the results differ so little from one another that we may feel justified in regarding the precise shape as relatively unimportant.

6. As a first approximation it will be presumably permissible to regard the molecule as a hard body formed by two overlapping hard spheres. In that case we may represent it by the full line figure in fig. 1. This figure actually shows to scale two argon atoms, but it will serve also to show qualitatively

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* These hard spheres apparently exert a slight mutual attraction, but this property is neither opposed nor essential to our present argument.

the other pairs. The atomic centres $O_1$ and $O_2$ lie in the plane of the diagram and are separated by the distance $2d$, *i.e.*, the diameter of the outer electron shell of each atom. The "kinetic theory" radius $\sigma$ of each hard atomic sphere being greater than $d$, a certain fraction of the space is common, and the resultant shape is a sort of shrunken dumb-bell. If we view this solid figure from a direction making an angle $\theta$ with the axis $O_1O_2$, it can be shown easily that the area $A_1$ presented is given by

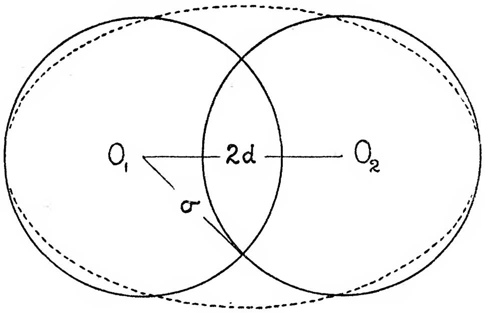

Fig. 1.

$$A_1 = 2\sigma^2(\pi - \phi + \cos\phi\sin\phi),$$

where $$\sigma\cos\phi = d\sin\theta. \qquad (2)$$

According to (1) the mean area presented for all possible orientations is

$$A_1 = 2\sigma^2 \int_0^{\pi/2} (\pi - \phi + \cos\phi\sin\phi)\sin\theta \, . \, d\theta \, . \, ,$$

which, with the application of relation (2) can be put in the form

$$\bar{A}_1 = \pi\sigma^2\left[1 + \frac{2K}{\pi}\int_0^{\pi/2}\{\cos^2\theta(1 - K^2\sin^2\theta)^{-\frac{1}{2}} + \sin^2\theta(1 - K^2\sin^2\theta)^{\frac{1}{2}}\}d\theta \, . \right]$$

where $$K = \frac{d}{\sigma}.$$

This can be evaluated in terms of complete elliptic functions with the result,

$$\bar{A}_1 = \pi\sigma^2\left[1 + \frac{4}{3\pi}\left\{\left(\frac{1}{K} + K\right)\mathbf{E}\left(K, \frac{\pi}{2}\right) - \left(\frac{1}{K} - K\right)\mathbf{F}\left(K, \frac{\pi}{2}\right)\right\}\right], \qquad (3)$$

from which, for any given value of K, $\bar{A}_1$ can be calculated in terms of $\pi\sigma^2$. Taking the values of K from Table I, $A_1$ has been in each case deduced and recorded in Table II, column 3.

7. I am indebted to Prof. S. Chapman for the suggestion that it has to be remembered that the sphere of radius $\sigma$ in the case of a single atom really represents a field of force, and that, therefore, when two such field interpenetrate the resultant field will be rounded off, so as not to exhibit the

discontinuity shown in the model just considered. He regards it as reasonable to represent the symmetrical diatomic molecule as an ellipsoid of revolution, having its long axis coincident with $O_1O_2$. If we attribute to such a spheroid semi-axes $a$ and $c$ ($a > c$), it is easy to calculate the mean area which it presents. Denoting by A the area presented when viewed in a direction making an angle $\theta$ with the major axis, we can show that

$$\mathrm{A} = \pi ac\left(1-\frac{a^2-c^2}{a^2}\cos^2\theta\right)^{\frac{1}{2}},$$

whence, by (1), and putting $p^2 = \dfrac{a^2-c^2}{a^2}$, which is of course less than unity,

$$\bar{\mathrm{A}} = \pi ac\int_0^{\pi/2}(1-p^2\cos^2\theta)^{\frac{1}{2}}\sin\theta\,.\,d\theta.$$

This integration is readily performed and we obtain

$$\mathrm{A} = \frac{\pi ac}{2p}\left(\phi_0+\tfrac{1}{2}\sin 2\phi_0\right), \tag{4}$$

where $$\sin\phi_0 = p = \left(1-\frac{c^2}{a^2}\right)^{\frac{1}{2}}.$$

8. We have now to subject this spheroid to the conditions necessitated by the proximity of the atomic centres. It is, in the first place, reasonable to suppose that the major axis of the spheroid is equal to the extreme length of the overlapping spheres in fig. 1, *i.e.*, that

$$a = \sigma+d. \tag{5}$$

The second condition is not so easy to specify. Two aspects seem to be equally worthy of consideration, and for this reason both have been included. If we assume that the volume of the spheroid is equal to the sum of the volumes of the two spheres, the condition is

$$ac^2 = 2\sigma^3. \tag{6}$$

Alternatively, if we assume that the volume of the spheroid formed by the joining of the two atoms is less than the joint volume by that which is common to the two spheres, the condition proves to be

$$ac^2 = \sigma^3\left[1+\tfrac{3}{2}\frac{d}{\sigma}-\tfrac{1}{2}\left(\frac{d}{\sigma}\right)^3\right],$$

or, remembering $$\mathrm{K} = d/\sigma,$$

$$ac^2 = \sigma^3\left(1+\tfrac{3}{2}\mathrm{K}-\tfrac{1}{2}\mathrm{K}^3\right). \tag{7}$$

The principal sections of the first of these two alternative spheroids, in relation to the overlapping spheres, is shown by the dotted line in fig. 1. The other lies inside, too closely to be represented conveniently.

Combining equations (5) and (6) with equation (4), and denoting by $\bar{A}_2$ the value of A under these conditions, we obtain

$$A_2 = \frac{\pi\sigma^2}{p_1}\left(\frac{1+K}{2}\right)^{\frac{1}{2}}(\phi_1 + \tfrac{1}{2}\sin 2\phi_1), \tag{8}$$

where

$$p_1^2 = 1 - \frac{2}{(1+K)^3} = \sin^2\phi_1\,;$$

whence the mean area presented by the spheroid of the first type can be calculated.

Similarly the combination of equations (5) and (7) with (4) give

$$A_3 = \frac{\pi\sigma^2}{2p_2}(1+K)^{\frac{1}{2}}(1+\tfrac{3}{2}K-\tfrac{1}{2}K^3)^{\frac{1}{2}}(\phi_2 + \tfrac{1}{2}\sin 2\phi_2), \tag{9}$$

where

$$p_2^2 = 1 - \frac{(1+\frac{3}{2}K-\frac{1}{2}K^3)}{(1+K)^3} = \sin^2\phi_2,$$

and $\bar{A}_3$ is the mean area presented by the spheroid of the second type.

The values of $A_2$ and $\bar{A}_3$ for the four gases in Table I have been calculated, and are recorded in columns 4 and 5 of Table II. It will be seen by comparison of $\bar{A}_1$, $A_2$, and $\bar{A}_3$, that the results obtained by the consideration of the three alternative models of the molecules are not large, the maximum difference being in the neighbourhood of 6 per cent. The importance of this will be considered later on.

Table II.—All areas in cm.$^2 \times 10^{-15}$.

| Gas. | $\pi\sigma^2$. | $\bar{A}_1$. | $\bar{A}_2$. | $\bar{A}_3$. | Gas. | S. | $\bar{A}_1$/S. | $\bar{A}_2$/S. | $\bar{A}_3$/S. |
|---|---|---|---|---|---|---|---|---|---|
| Ne ............... | 0·435 | 0·67 | 0·70 | 0·65 | $O_2$ .............. | 0·69 | 0·97 | 1·02 | 0·94 |
| A.................... | 0·648 | 1·08 | 1·06 | 1·03 | $Cl_2$ .............. | 1·07 | 1·01 | 0·99 | 0·96 |
| Kr ............... | 0·797 | 1·34 | 1·31 | 1·28 | $Br_2$ .............. | 1·28 | 1·05 | 1·03 | 1·00 |
| X ............... | 0·970 | 1·66 | 1·60 | 1·57 | $I_2$.................. | 1·56 | 1·06 | 1·03 | 1·00 |

9. It is now possible to carry out comparisons with experimental results. In column 7 of Table II, I have recorded the effective mean areas (S) of the diatomic molecules $O_2$, $Cl_2$, $Br_2$, and $I_2$, using Chapman's formula and the best available viscosity data. For oxygen I have taken Chapman's own estimate, which is in remarkably close agreement with that which may be deduced from the recent viscosity measurement by Kia Lok Yen* in Millikan's laboratory. In the case of the halogen gases, I have used the data from my own experiments,† these being the only measurements avail-

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* Kia Lok Yen, 'Phil. Mag.,' vol. 38, p. 582.

† A. O. Rankine, 'Roy. Soc. Proc.,' A, vol. 86, p. 162; vol. 88, p. 575; and vol. 91 p. 201.

able. The last three columns show the respective values of the ratios $\bar{A}_1/S$, $\bar{A}_2/S$, and $\bar{A}_3/S$, and it will be noted that all these ratios are remarkably close to unity. The significance of this is important. It means that, for example, two argon atoms, with their outer electron shells coincident, would have a field of force which is almost identical with the actual field of force for a chlorine molecule, with the consequent deduction that the chlorine and argon atoms have equal size and shape. A similar argument applies to each pair of corresponding monatomic and diatomic gases.

10. It is worth while considering how the departures from unity in the ratios $\bar{A}/S$ may be accounted for. The maximum difference, whichever model we consider, is 6 per cent., and, if we confine our attention to the second model, *i.e.*, the spheroid of major axis $2(d+\sigma)$ and volume $\frac{8}{3}\pi\sigma^3$, the departure is reduced to a maximum of 3 per cent. It is quite possible that this may be accounted for by inaccuracy of the data upon which the calculations are based. Altogether apart from possible error in W. L. Bragg's figures, the calculation of S for the halogen gases, at any rate, is certainly liable to be inaccurate by a few per cent. For these gases, the viscosity measurements were, owing to experimental difficulties, carried out below the critical temperatures, that is, in a region of temperature where the kinetic theory of gases admittedly becomes inadequate. This consideration applies especially to bromine and iodine, in which cases it would alone, I think, account for the inconsistency in question. It is possible, also, that some allowance ought to be made for the distortion of the electron shells in atoms when they join to form molecules. Bearing these facts in mind, there seems to be considerable justification provided by the present investigation for making the following assertions:—

(*a*) There is substantial quantitative consistency between the estimates of atomic dimensions deduced from X-ray crystal measurement and from the kinetic theory of gases.

(*b*) In size and shape, the atoms of the monatomic inert elements are nearly indistinguishable from the atoms, respectively, of the neighbouring diatomic elements in the periodic table.

(*c*) The Lewis Langmuir molecular theory accounts satisfactorily for the kinetic behaviour of the molecules of oxygen, chlorine, bromine, and iodine in relation to the behaviour of the corresponding inert atoms, neon, argon, krypton, and xenon.

11. It has been already mentioned that the best model of the hard elastic body to which a molecule composed of two equal atoms is equivalent is a spheroid. The volume of this spheroid is equal to the sum of the volumes of the hard elastic spheres to which each participating atom is

separately equivalent. Apparently, the fields of force of the atoms, when they interpenetrate, rearrange themselves by bulging out in the equatorial plane, and contracting somewhat towards the poles, so as to preserve the same effective total volume. The other spheroid model, in which the total volume is diminished by the over-lapping volume, is not quite so successful. But both it, and more particularly, the first simple model contemplated (*i.e.*, a pair of overlapping spheres) give results which are reasonably consistent. This is fortunate, for it makes it possible to place some confidence in the extension of present theory to molecules in which the atoms are not equal. In that case the spheroid is an unlikely model, but we may still obtain results by methods, admittedly more laborious, based upon the model of overlapping spheres. This investigation the author hopes to carry out.

12. The case of nitrogen deserves special consideration. The molecule of this gas ($N_2$) has not been included in the above comparison because, according to Langmuir's theory, it is formed from two nitrogen atoms in a peculiar way. Each atom of nitrogen, if it could exist singly, is regarded as having only five electrons in the outer shell instead of the eight required to complete the stable neon arrangement. Langmuir represents these eight electrons as forming an octet or cube, and the joining of pairs of fluorine atoms to form $F_2$, or pairs of oxygen atoms to form $O_2$, by sharing electrons, presents no difficulty. In the former case, the deficiency of electrons being one per atom, the fluorine molecule attains the shape of two neon atoms in contact by the two shared electrons forming the common edge of the two cubes. In the oxygen molecule four electrons have to be shared by the atoms, and here the two cubes have a common face. With a deficiency of three electrons, however, as in the case of nitrogen, it is impossible for six electrons to be held in common without the complete disappearance of the linked neon cubes. In these circumstances, Langmuir regards the formation of the nitrogen molecule as being fundamentally different from the corresponding process in oxygen and fluorine. The interpenetration of the atoms is taken to be far greater, and involves a complete rearrangement of the electrons. The actual model given by Langmuir is a *single* enlarged electron cube of eight with *both* positive nuclei inside it. It is evident that this molecule has no resemblance at all to a pair of linked neon atoms, and it is most unlikely that its field of force, from the point of view of kinetic theory, will conform to any of the models we have considered. Indeed, if Langmuir's view is correct, a nitrogen molecule would be equivalent to a hard elastic body nearly spherical in shape, and the unmodified kinetic theory would apply to it with the same precision

as in the case of monatomic gases. Its atomic diameter, deduced from the viscosity of the gas, is $3 \cdot 13 \times 10^{-8}$ cm., which makes its mean area $S = 0 \cdot 78$ cm$^2 \times 10^{-15}$. This is considerably larger than any of the values of $\bar{A}$ for neon (Table II), and points to the fact that a nitrogen molecule does not resemble two linked neon atoms. In this negative sense, therefore, we again have corroboration of Langmuir's theory. For both points of view indicate that, whatever may be the actual arrangement of the nitrogen molecule, its mode of formation from two atoms is essentially different from that of its neighbour, the oxygen molecule.

13. In conclusion, I wish to express my gratitude to Prof. S. Chapman for reading the draft of this paper, and for making the suggestion—already referred to—which I have adopted.

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# On the Similarity between Carbon Dioxide and Nitrous Oxide.

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1. One of the most remarkable evidences in favour of the Lewis-Langmuir* theory of molecular constitution is the close degree of equality between nearly all of the physical constants of the two compounds, carbon dioxide and nitrous oxide. This identity is attributed by Langmuir to the arrangement of external electrons being the same for the molecules of the two gases in question. It is the purpose of the present communication to show that an appeal to the kinetic theory of gases, in conjunction with what is now known from W. L Bragg's† work regarding the dimensions of atoms, produces substantial additional evidence in support of the Lewis-Langmuir views. In particular, it will be shown that the molecules of $CO_2$ and $N_2O$ behave not merely as though they had the same size and shape, but as if each of them had an external electron arrangement practically the same as that of *three neon atoms in line and contiguous.*

2. This arrangement is precisely that which Langmuir suggests and is represented in fig. 1. A single neon atom is pictured as having eight outer

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* I. Langmuir, 'Journ. Amer. Chem. Soc.,' vol. 41, p. 868 (1919).

† W. L. Bragg, 'Phil. Mag.,' vol. 40, p. 169 (1920).